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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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TITLE OF THE INVENTION (500 characters max)

CLONING SINGLE WALL CARBON NANOTUBES FOR HYDROGEN STORAGE

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ENCLOSED APPLICATION PARTS (check all that apply)



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Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT



Applicant claims small entity status. See 37 CFR 1.27.



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Respectfully submitted,

SIGNATURE

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Date

10/14/2003

REGISTRATION NO.

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Docket Number:

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CLONING SINGLE WALL CARBON NANOTUBES FOR HYDROGEN STORAGE

SUMMARY

Of all carbon materials, single wall carbon nanotubes (swnt) provide the highest possible surface to mass ratio, as well as access to both the inner and outer surfaces of open-ended swnt. In principal, because of its surface to mass ratio, swnt should be the best possible carbon material for hydrogen storage.

However, issues of hydrogen accessibility to all of the potential surface of swnt, the extent of hydrogen coverage that is attainable, the dependence of coverage on the nature of hydrogen bonding, the facility with which hydrogen is transported on and off of the swnt, and the role that nano-metal particles can play in promoting hydrogen adsorption will impact the use of swnt as a hydrogen storage material.

In addition, there is the likelihood that the strength of hydrogen adsorption and covalent bonding of hydrogen to the sidewall of carbon nanotubes is strongly dependent on the curvature of individual nanotubes. Interaction of hydrogen may also be sensitive to swnt chirality and whether they are predominantly metallic or semiconductor in character.

Since a given swnt is a well-defined molecular carbon polymer, scalable chemical strategies have been and are being developed by other groups at Rice and elsewhere [Billups *et al.*, *Org. Letters*, 5, 1471, (2003), Tour *et al.*, *J. Am. Chem. Soc.*, 123, 6536, (2001), Haddon *et al.*, *Science* 1501, (2003)]. Sidewall functionalization provides spacer groups on the sidewalls of swnt that expand the super-lattice of the nanotube bundles and ropes, thus providing gas accessibility. These same functional groups can also serve as sites for adsorption of catalytic metals at the atomic level to provide low activation pathways for transport of hydrogen to and from the surface of swnt.

The present invention is directed towards a method of providing large quantities of swnt of defined diameter and chirality, wherein some of these diameters and chiralities are ideally suited for hydrogen storage. This is accomplished with a process referred to herein as "cloning." In this process, swnt seeds of a pre-selected diameter and chirality are grown to hundreds of times their original length. This is followed by cycling some of the newly grown material as seed material for regrowth. Thus, the present invention provides for the production of swnt in kiloton amounts at reasonable cost, and which can be optimized for hydrogen storage.

The initial process of cloning involves cutting swnt produced in Applicants' existing HiPco reactor at Rice University, Houston, Texas. Tubes that are microns in length can be cut to tens of nanometers. The cut tubes are prepared for growth by attaching a nanometer catalyst to their ends to form "seeds." Re-growth can then be carried out with swnt seeds dispersed on supports or by injection of seeds into the gas phase of a growth reactor.

Thus, the cloning process of the present invention is broken down into a series of steps: cutting, sorting by type, docking of prepared cut tubes and metal catalyst particles, growth of SWNT on supports or as dispersed seeds in a growth gas environment.

DETAILED DESCRIPTION

The challenge for hydrogen storage with carbon materials is to produce a carbon material that meets hydrogen-to-carbon volumetric and weight storage ratios at near-ambient temperature that are suitable for efficient and cost-effective use with mobile vehicles (e.g., freedom car).

Of all carbon materials, single wall carbon nanotubes, swnt, provide the highest possible surface-to-mass ratio, along with accessible inner and outer molecular surfaces using open-ended swnt. In principal, because of their high surface-to-mass ratio, swnt are probably the best possible carbon material for hydrogen storage.

However, for swnt to be a cost-effective solution for hydrogen storage, they must be made in ton quantities, preferably with a diameter and chirality that is optimized for hydrogen storage. All current methods of growing swnt require that swnt be nucleated on a metal particle before growing. It is very likely that the best temperature for nucleation, which requires formation of a "fullerene cap," is at least a few hundred degrees higher than the best temperature for growing nanotube cylinders. Additionally, nucleation is typically a low-probability event. As a result, most metal nanoparticles simply coalesce to form larger particles that are invariably overcoated with carbon "onions."

While not intending to be bound by theory, it is believed that yields and production rates of swnt can be greatly increased by separating nucleation from growth. The present invention provides a method by which the separation of the nucleation and growth processes is accomplished by using swnt seeds obtained from swnt that has been cut into short (10-20 nm) pieces. Growth from seeds provides for the growing of swnt of specific diameter and chirality when the seeds have been presorted by diameter and chirality. This process is referred to as cloning single wall carbon nanotubes.

Numerous studies of physisorbed molecular hydrogen on swnt have had widely varying results, undoubtedly due in part to variations in swnt structures and various defects. [ref. M. D. Ward, *Science*, 300, 1104 (2003)]. The persistence of some H₂ uptake in most studies indicate that there are some sites and/or nanotube structures that successfully adsorb H₂, most likely involving some degree of charge transfer, and that so far the creation of such sites is hit-or-miss empiricism, [ref. R. Dagani, *C&E News*, 80(2), 25 (2002)]; hence nanotubes must be tailored for optimum interaction with hydrogen.

Dissociative chemisorption provides much stronger attachment to swnt by C-H covalent bonding. Long-known catalytic "spillover," whereby the dissociated hydrogen migrates to the host carbon is the key. Very recently, this has been extended to multi-wall nanotubes (mwnt) using a nanodispersed

catalyst, [ref. A Lueking and R T Yang, *J. Catal.* 206, 165 (2002)], and theoretically studied [ref. F H Yang and R T Yang, *Carbon*, 40, 437, (2002)]. However, many carbons are hidden in mwnt, limiting the storage capacity; whereas for a swnt, all carbons are equivalent and accessible, for maximum possible hydrogen storage. A nanodispersed spillover catalyst will add only minimal weight.

Note, however, that applications for "cloned" swnt produced in large quantities will not be limited to use in hydrogen storage. Many applications exist for swnt of precisely-defined diameter and chirality. These include, but are not limited to, chemical sensors, medical diagnostic/therapeutic applications, microelectromechanical systems (MEMS), nanoelectromechanical systems (NEMS), and combinations thereof.

For example, cloning single wall carbon nanotubes can be accomplished by a series of steps comprising:

1. Cutting single wall carbon nanotubes;
2. Sorting single wall carbon nanotubes;
3. Preparation of cut tubes and metal catalyst precursor for docking;
4. Attachment of catalysts to cut tubes;
5. Reductive docking of catalysts to cut tubes;
6. Growth of seeds on supports; and
7. Growth of seeds by injection into gas environment.

Cutting single wall carbon nanotubes

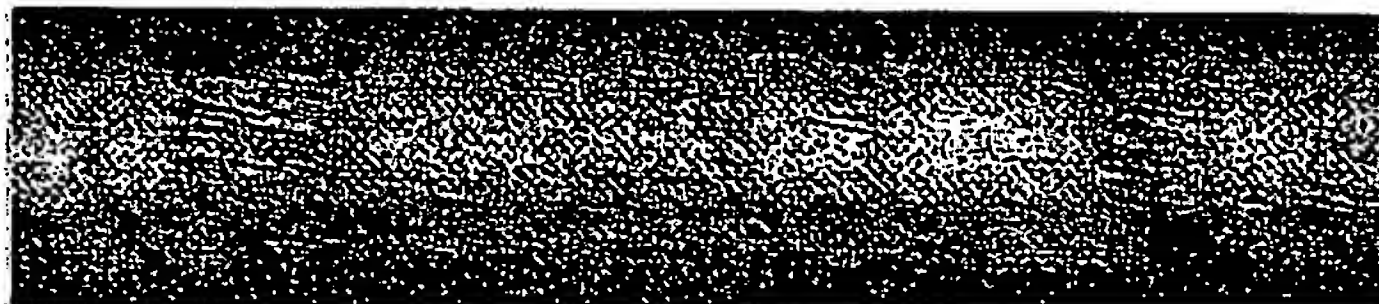
Cutting processes for swnt, that can be utilized for the present invention, are ideally low-cost, efficient and scaleable to multi-kilogram quantities. A characteristic of swnt is that the fundamental tubes bind into long ropes of ~30 to 200 nm diameter. Thus, many nanotubes are not accessible to chemicals that do not penetrate the swnt-rope super-lattice. A requirement for cutting processes is that the chemicals have to be able to access the sidewalls of all nanotubes. Thus, for efficient cutting, nanotubes must be dispersed as individuals or the chemicals must be able to penetrate into the rope super-lattice. Alternatively, the rope super-lattice may be expanded with sidewall functionalization so that reactive chemicals will penetrate the ropes.

Cutting can occur anywhere along the length of a nanotube, not only at sidewall defect sites. Experience has shown that free radicals readily add to the sidewalls of swnt. Thus, chemicals most useful in cutting are those that react through a free radical mechanism and ultimately produce soluble or volatile carbon species.

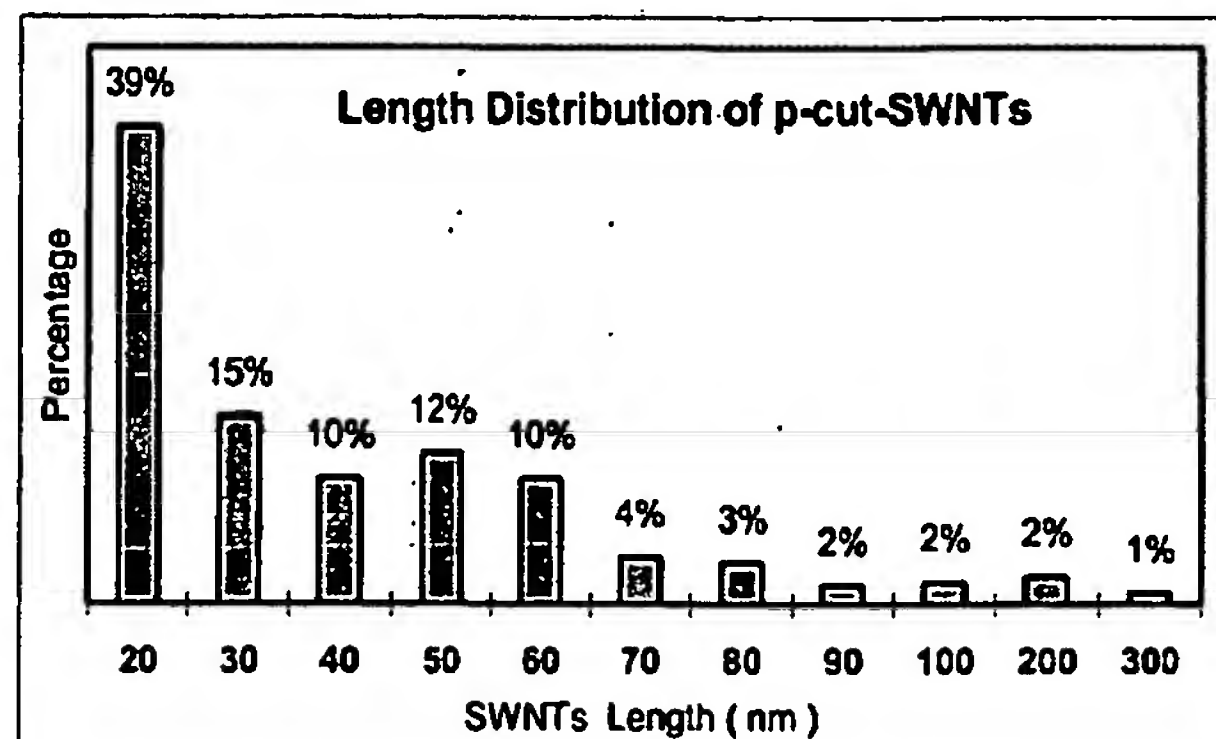
Two gaseous reagents that can be used in cutting swnt are elemental fluorine and ozone. Fluorine has the advantage of being able to penetrate into ropes in a manner similar to the way it intercalates into graphite. [Margrave *et al.*, *Nano Lett.* 2, 1009, (2002)]. Ozone does not penetrate into the rope superlattice, but does react at room temperature with nanotubes on rope surfaces. Cutting processes that use ozone require that nanotubes be pre-dispersed or that the rope lattice be expanded via sidewall functionalization.

Direct fluorination of swnt has been shown to readily access all nanotubes in a rope. Other chemicals that are also known to intercalate graphite such as sulfuric acid, and superacids may be useful as cutting agents or as carriers for cutting agents.

Fluorination of swnt has been shown to occur in bands as is illustrated in the adjacent AFM scan [Halas *et al.*, *Chem. Phys. Lett.* 313, 445, (1999)].



When partially fluorinated swnt is heated to $\sim 600^\circ\text{C}$ many short lengths of nanotubes are formed as a result of the gasification of the fluorinated regions. The following figure provides a graph of the lengths that result from heating partially fluorinated swnt. Clearly, cutting is extensive and lengths of tens of nanometers are readily obtained.



Recent work by Applicant has shown that individual swnt, roughly one micron in length, can be obtained with intense sonication of swnt in surfactant-water mixtures. This has led to a much better understanding of the dependence of electronic structure on nanotube chirality. Recent work by Applicant has also shown that individual nanotubes in a surfactant-water suspension can be cut with ozone. However, cutting from such a process has not been shown to be as extensive as with fluorine.

Extensive sidewall functionalization of nanotubes has been recently accomplished using chemical methods that produce intermediate free radical species. [ref. Billups *et al.*, *Org. Letters* 5, 1471, (2003), Tour *et al.*, *J. Am. Chem. Soc.* 123, 6536, (2001).] Furthermore, such methods appear scalable to kilogram quantities. Thus, in some embodiments, functionalized swnt with a lattice structure that is open (by virtue of having been sidewall functionalized) to infusion of oxidants such as ozone provide alternative routes to cutting. While not intending to be bound by theory, ozone is believed to react primarily with areas that are not sterically protected by functional groups.

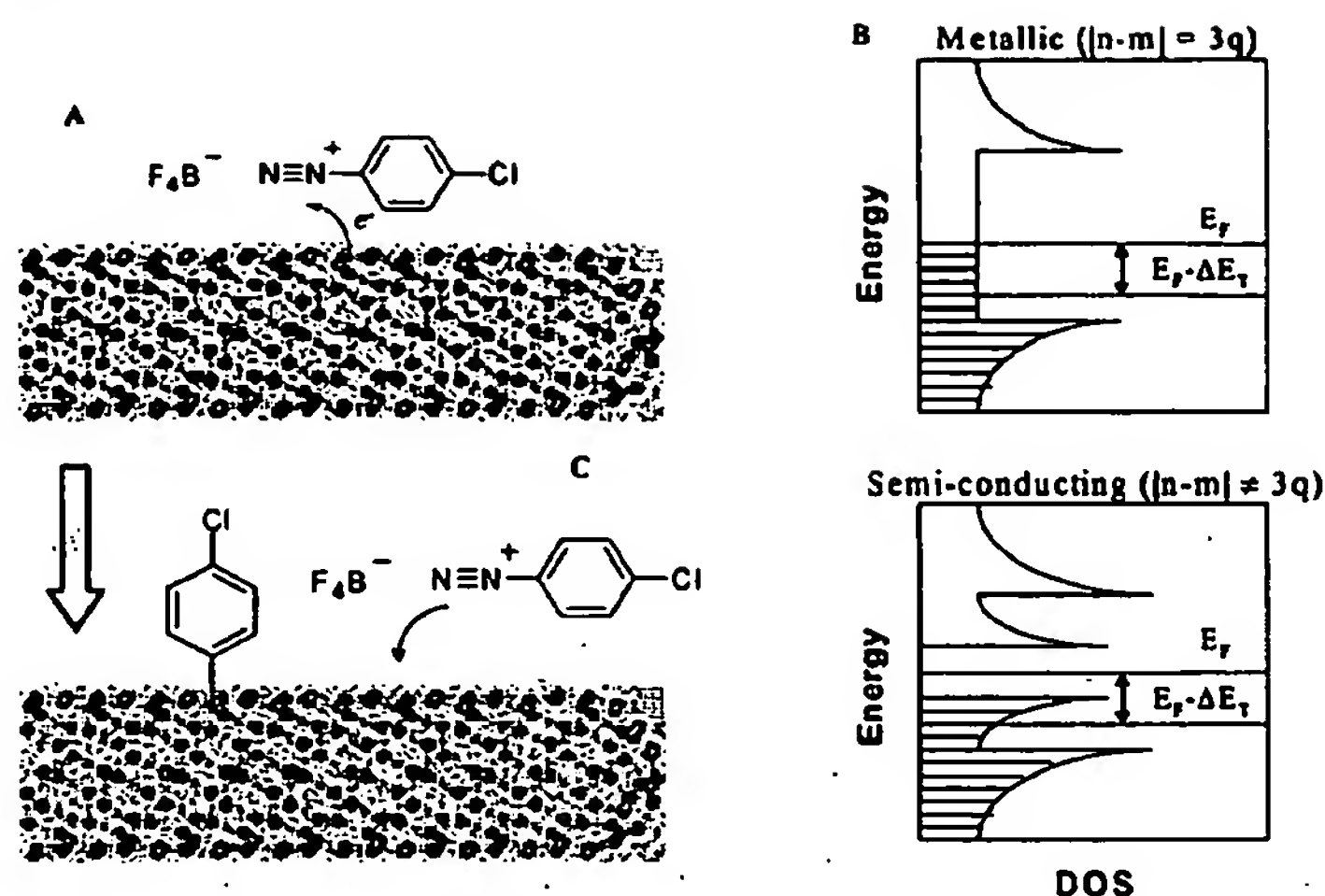
Sorting single wall carbon nanotubes

Sorting the carbon nanotubes by type can be utilized for supplying the seeds that are to be scaled up into large quantities of identical cloned nanotubes.

Although at first glance, it might be thought that the curved graphene sheet will present rather similar sidewalls to approaching reagents, differentiated only by strain energy, a considerable difference in reactivity has been observed in a number of ways, including something as simple as a response to changing acid/base in micelle/water suspensions, swnts each exhibit their own personalities.

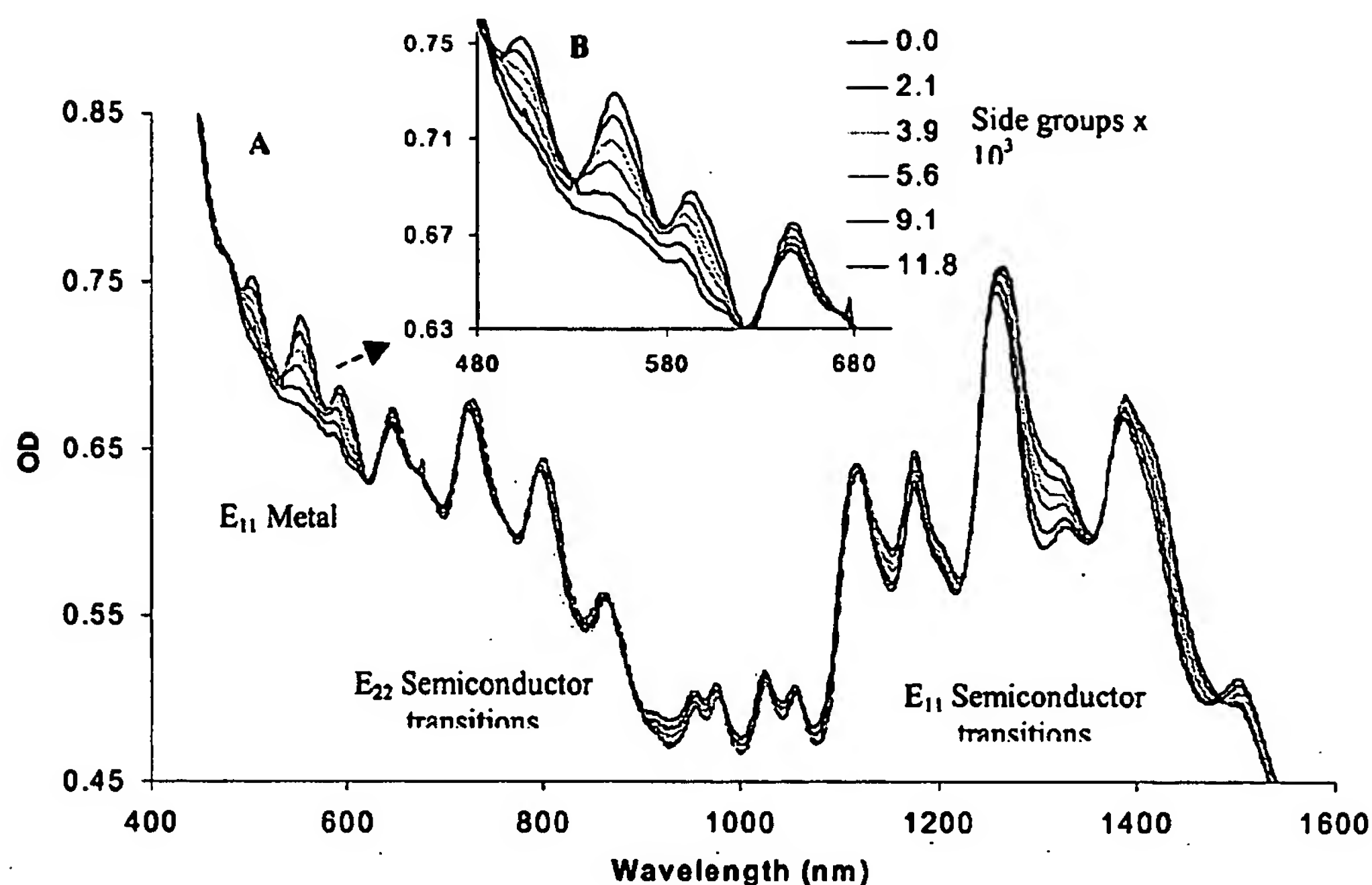
The dominant factor in sidewall reactivity in many cases turns out to be the availability of electrons for donation by the swnt. For mod 3 residual = zero, or metallic swnt, there are levels that cross the Fermi level, and electrons are readily available. For mod 3 residual = 1 or 2, or semiconductor swnt, the highest lying electrons are in the van Hove valence bands typically 1/2 eV or more below the Fermi level. In addition, larger diameter swnt show longer wavelength absorption, indicating the van Hove singularity is closer to the Fermi level. Thus, reactants that depend on the availability of electrons can be made to selectively attack the nanotube sidewalls. Aryl diazonium salts are one such class of reactants, as shown in the following figure. As this moiety migrates to the surface of the swnt, the positive charge on the nitrogen end attracts an electron from the nanotube, which stabilizes the transition state as the nitrogen molecule departs. Then the remaining aryl radical attacks the sidewall and forms a covalent bond:

Figure 1



As this moiety migrates to the surface of the swnt, the positive charge on the nitrogen end attracts an electron from the nanotube, which stabilizes the transition state as the nitrogen molecule departs. Then the remaining aryl radical attacks the sidewall and forms a covalent bond.

The readily available electron from the metallic swnt makes this reaction much faster than for the semiconductor swnt, hence with measured addition of the reagent, essentially only the metallic swnts will become derivatized. The strain of the first side group makes adjacent carbons more reactive, and so the nanotube continues to load up on derivatives. [ref. Strano *et al.*, *Science* 301, 1519, (2003)]. The result is a remarkable and essentially total selective functionalization of the metallics [swnt], whereas the semiconductors are virtually untouched. This is readily seen in the absorption spectra of the solution, as shown in the following figure, where the metallic absorption peaks ca. 500 nm are flattened, but the first van Hove absorption features of the semiconductors in the near IR are hardly affected. In addition, the Raman radial breathing mode (RBM) spectra show some propensity for further selective derivatization within the metallic group



Selective derivatization leads to sorting. The functionalization improves the solubility in solvents such as DMF, so the metallic swnts may be extracted. In addition, reactive functional groups may be attached to the tails of the aryl derivatives, which in turn can be attached to, *e.g.*, water soluble polymers that will keep those nanotubes in suspension when the micelle-forming matter is removed and the insoluble semiconductors precipitate out.

Scale-up using a continuous flow sonicator has been recently shown by Applicants to effectively derivatize swnt with the previously mentioned diazonium chemistry, bypassing a tedious centrifuge step. This allows the process to be scaled up to larger amounts. Since the cloning of seeds bootstraps the production of the selected type of swnts, exceptionally large volume sorting is generally unnecessary.

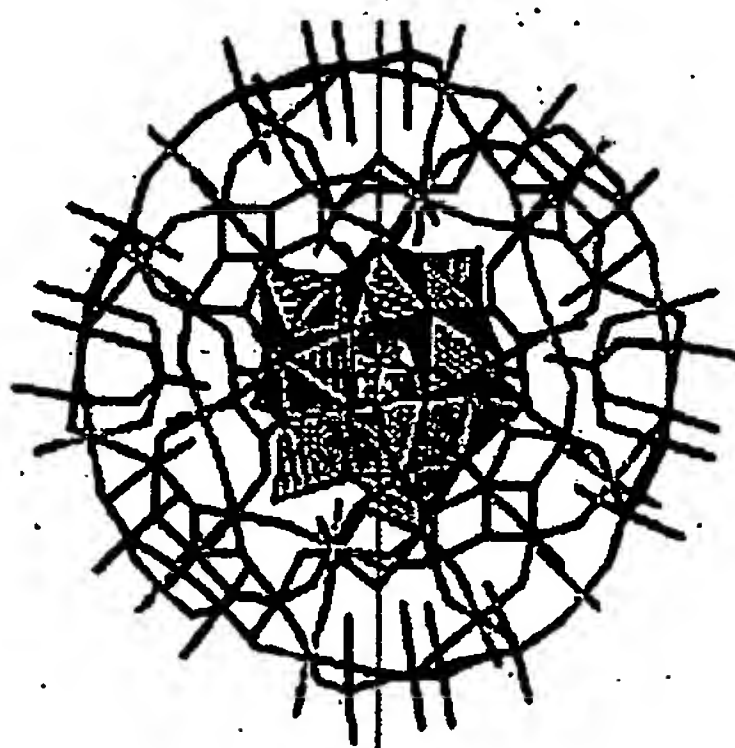
In other embodiments, sorting is accomplished by a sequential "protonation" of semiconductor nanotubes, starting with the largest, so that chiral selectivity within the semiconductor group appears reasonable. Once the metallic swnt are removed, semiconductor swnt of different diameters can be selectively functionalized with diazonium chemistry.

Other embodiments employ a superacid, e.g., chlorosulfonic acid, in the sorting process. The acid interaction with the nanotube sidewall appears to exhibit dependence on the availability of electrons and, correspondingly, chirality and diameter. A superacid extraction of swnt material shows some chirality differentiation between the extract and the residue. The advantage here is that the acid can be removed with vacuum distillation leaving nanotubes enriched in metallic swnt. This separation process is of interest because of its simplicity and easy scalability.

In some embodiments, the swnt are also sorted by length using one or more of the following techniques: chromatography, electrophoresis, filtration, and centrifugation.

Preparation of cut tubes and metal catalyst precursor for docking

As an exemplary metal catalyst precursor, a molecular cluster that contains molybdenum and iron, $\text{Fe}_{30}\text{Mo}_{70}$ has been recently shown to be an excellent catalyst for SWNT growth by J. Liu (Duke) [ref. J.Liu *et al.*, *JACS*. Accepted, (2003)]. The iron molybdate cluster, (FeMoC) is a keplerate cation around a central Mo_{12}P Keggin anion, [ref. Muller, *Angewandte Chemie Int. Ed.* 39, 3417, (2000).] The figure below illustrates the iron-molybdenum oxide cage surrounding the inner Mo_{12}P Keggin anion. The net charge on the cluster is zero.



The cluster is soluble in water and has 60 water molecules coordinated to metal ion sites. It is soluble in water and methanol as well as some organic solvents such as dimethylformamide (DMF). It is believed that water can be displaced from the coordination sphere with amine groups. The cluster appears to be ideally suited for docking to cut SWNT seeds. It is easily made and stable for long periods of time in water. Other molecular clusters similar to FeMoC and comprising suitable metal species can also be used as metal catalyst precursors.

In some embodiments, docking to the ends of cut nanotubes can be as simple as the displacement of coordinated water with carboxylic groups present on the open ends of cut tubes. Alternatively, the cut tube ends can be functionalized with groups that are terminated by an amine group.

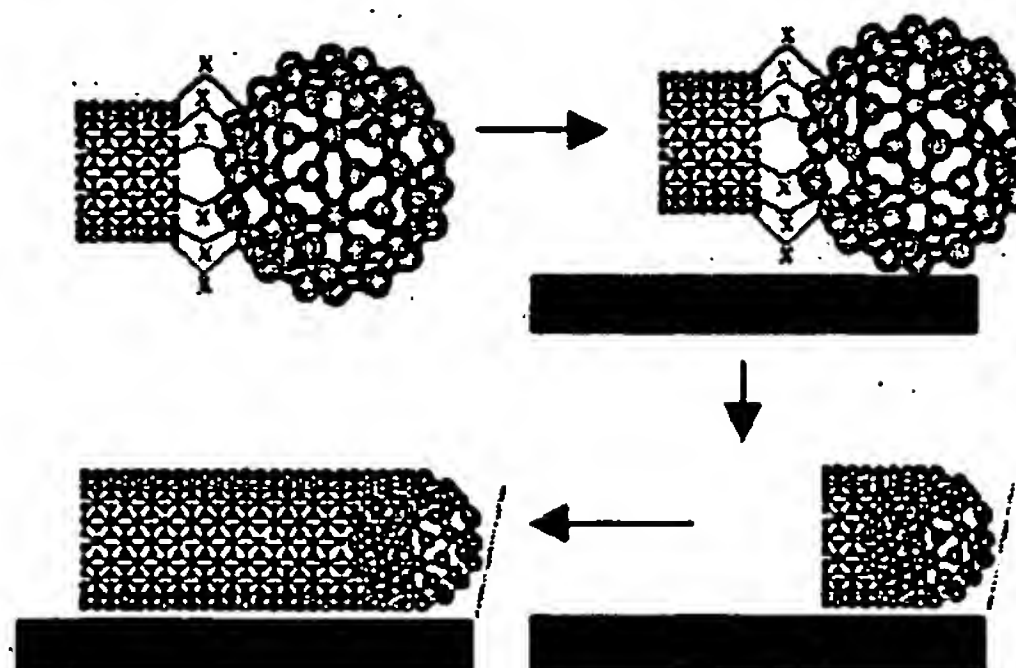
Preparation of the ends of cut tubes involve opening the ends of the cut tubes if they were not already opened in the cutting process, and ensuring that carboxylic groups exist on the ends of the tubes. Carboxylic groups can be readily functionalized with standard organic chemical methods.

Attachment of catalysts to cut tubes and reductive docking

The ability to grow nanotubes from seeds depends on having a highly efficient method for docking a nanometer sized metal cluster to the ends of cut nanotubes. This requires that all cut nanotubes are accessible for end chemistry. The best way to ensure access is to extensively functionalize the sidewalls of seeds with a group that gives good solubility in a variety of organic solvents. Recent free radical chemistry developed at Rice University has demonstrated that excellent solubility is achieved for swnt when it is fully functionalized. Standard organic reactions can be applied to the end groups of the cut tubes to create amine-terminated or other groups that have a favorable interaction with the FeMoC metal cluster previously mentioned. The FeMoC clusters can also be functionalized to further enhance selective docking to the ends of cut nanotubes. The procedures allow clusters that are not docked to be washed away leaving only metal clusters that are docked to nanotube seeds. Docking can be confirmed with cryoTEM. The docked clusters can then be reduced to the metallic state in a reducing environment such as hydrogen.

Growth of seeds on supports

The growth of swnt from seeds is illustrated in the figure below. In this case, a nanotube seed with its docked catalyst particle is dispersed on a support. The seed is then exposed to a reducing atmosphere in order to reductively dock the metal oxide particle to the end carbon atoms of the nanotube. This will eliminate any possibility of spontaneous nucleation. The docked seeds are subsequently grown in a carbon rich environment such as CO and H₂ at one atmosphere and 700 °C.



In some embodiments, the growth of seeds is carried out on a silicon wafer substrates where the growth of specific seeds can be monitored with atomic force microscopy (AFM). In other embodiments, the substrate is selected from the group consisting of silica, alumina, magnesium oxide, and combinations thereof. Cut nanotubes with a docked catalyst particle can be dispersed on fumed alumina, commercial nano-titanium dioxide, and high surface area magnesium oxide. In order to enhance the dispersion of seeds, metal oxide surfaces can be coated with amine-terminated functional groups that will bind to the metal cluster and pin the nanotube seeds to the support surface.

Growth of seeds by injection into gas environment

Direct injection of nanotube seeds into a hot carbon rich gas stream where the seeds are rapidly dispersed as individuals in the hot reactor gas provides for a scalable growth process.

Since the seeds are not volatile they must be transported into the reactor by a liquid stream in which they are solubilized or suspended. However vaporization of micron-sized liquid droplets can cause agglomeration of the seeds present in the droplet. In some embodiments, a solution to this problem is the use of supercritical CO₂ as the liquid carrier, wherein the seeds are individually suspended in a surfactant or dispersed on nano-oxide particles. In other embodiments, aggregation can be prevented with a form of electrospray, so that particles fragment rather than grow due to charge repulsion as they form.

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WHAT IS CLAIMED IS:

1. A process comprising the steps of:
 - a) providing a plurality of swnt;
 - b) cutting the swnt to provide cut swnt comprising lengths on the order of tens of nanometers;
 - c) sorting the cut swnt by type to provide sorted cut swnt;
 - d) docking the sorted cut swnt to metal catalyst precursors to form swnt seeds; and
 - e) growing the swnt seeds to form a swnt product of increased length.
2. The process of claim 1, further comprising a step of cycling some of the swnt product back into the process.
3. The process of claim 1, wherein the swnt are cut by a method selected from the group consisting of partial fluorination, selective ozonation, superacid treatment, and combinations thereof.
4. The process of claim 1, wherein the cut swnt are sorted by a method selected from the group consisting of selective chemical functionalization, selective protonation, superacid extraction, and combinations thereof.
5. The process of claim 1, wherein the metal catalyst precursor is a molecular cluster comprising a suitable metal catalyst.
6. The process of claim 1, wherein docking the sorted cut swnt to the metal catalyst precursor comprises a displacement of coordinated water molecules with carboxylic groups on the swnt ends.
7. The process of claim 1, wherein docking the sorted cut swnt to the metal catalyst precursor further comprises reducing the metal catalyst precursor to its metallic state in a reducing environment.

8. The process of claim 1, wherein the growth environment comprises a support.
9. The process of claim 1, wherein placing the swnt seeds in a growth environment comprises an injection process.
10. The process of claim 1, wherein the growth environment comprises CO and H₂.
11. A process comprising the steps of:
 - a) providing a plurality of swnt, wherein substantially all of the swnt are of a pre-selected chirality and diameter;
 - b) forming swnt seeds from the plurality of swnt;
 - c) growing the swnt seed to provide a swnt product comprising increased length swnt of the pre-selected chirality and diameter.
12. The process of claim 11, wherein the swnt product is utilized for hydrogen storage.

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PROVISIONAL PATENT

APPLICATION DATA SHEET

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